was subjected to initial fractionation on a Si gel column. The flavonoid containing fraction (2.0 g) was eluted by 30% EtOAc–C_6H_6. TLC indicated the presence of two components R_f 0.7 (AO-1) and R_f 0.11 (AO-2) (Solvent A). Column chromatographic separation of the two components was effected on Si gel using EtOAc–C_6H_6 (10 and 20%) as eluent.

AO-1 (*naringenin*). Yield 0.5 g, pale yellow needles (EtOAc–C_6H_6), mp 255–257°. It was found to be identical with naringenin.

AO-2 (*naringenin-7-O-(6″-O-p-coumarryl)-β-D-glucoside*). Yield 0.5 g, pale yellow cubes, mp 153–154°. (EtOAc–C_6H_6) UV (MeOH) 212, 226, 285, 314 nm; (MeOH + NaOAc) 285, 320, 360 (*sh*) nm; (MeOH + NaOMe) 240 (*sh*), 288, 364 nm. IR (KBr): ν cm^{-1} = 3300 (OH), 1675 (CO_2R), 1625 (C=O), 815 (Ar) NMR: (^{1}H, DMSO-d_6 + TFA-d, TMS int.) δ = 7.59 ppm (*d*, 1H, *J* = 16 Hz, H-β), 7.55 (*d*, 2 H, *J* = 9 Hz, H-2‴, H-6‴), 7.35 (*d*, 2 H, *J* = 8.5 Hz, H-2′, H-6′), 6.83 (*d*, 4 H, *J* = 9 Hz, H-3′, H-3‴, H-5′, H-5‴), 6.63 (*d*, 1 H, *J* = 16 Hz, H-α), 6.22 (*s*, *br*, 2H, H-6, H-8) 5.50 (*d*, 1 H, *J* = 12 Hz, H-2), 5.13 (*d*, *br*, 1 H, *J* = 6 Hz, H-1″), 4.31 (*m*, 2 H, H-6″, H-6‴), 2.70–4.15 (*m*, 6 H, H-3, H-3, H-2″, H-3″, H-4″, H-5″). NMR: (^{13}C, DMSO-d_6, TMS int.) δ = 197.2 ppm (C-4), 166.4 (C-9‴), 165.0 (C-7), 163.0 (C-5), 162.6 (C-9), 159.8 (C-4‴), 157.7 (C-4′), 144.9 (C-8‴), 130.3 (C-2‴, C-6‴), 128.6 (C-1′), 128.4 (C-2′, C-6′), 125.0 (C-1‴), 115.7 (C-3‴, C-5‴), 115.1 (C-3′, C-5′), 113.9 (C-7‴), 103.3 (C-10), 99.2 (C-1″), 96.3 (C-6), 95.5 (C-8), 78.6 (C-2), 76.1 (C-3″), 73.8 (C-5″), 72.9 (C-2″), 69.8 (C-4″), 63.3 (C-6″), 42.0 (C-3).

Prunin-chalcone-6″-p-coumarate-PME. AO-2 (2 mg) was permethylated using NaH/MeI in DMF and worked up as usual [4]. MS $C_{37}H_{42}O_{12}$ (678.72) *m/e* 678 M$^+$ (21% rel. int.) 650 (12), 517 (8), 432 (17), 365 (84), 364 (58), 314 (100), 315 (36), 299 (71), 286 (90), 187 (54), 178 (77), 161 (500), 155 (85), 153 (92), 141 (65), 134 (130), 133 (92), 121 (86), 120 (45), 111 (30), 101 (110), 91 (61), 89 (65), 71 (95), 45 (78).

Hexa-acetate of AO-2. The acetylation was carried out with Py–Ac_2O for *ca* 18 hr at room temp. and worked up as usual and crystallized from $CHCl_3$, mp 115°. NMR (^{1}H, $CDCl_3$, TMS int.) δ = 7.72 (*d*, 1 H, *J* = 16 Hz, H-β), 7.57 (*d*, 2 H, *J* = 8.5 Hz, H-2‴, H-6‴), 7.46 (*d*, 2 H, *J* = 9 Hz, H-2′, H-6′), 7.19 (*d*, 4 H, *J* = 9 Hz, H-3′, H-5′, H-3‴, H-5‴), 6.60 (*d*, 1 H, *J* = 2.5 Hz, H-8), 6.43 (*d*, 1 H, *J* = 2.5 Hz, H-6), 6.41 (*d*, 1 H, *J* = 16 Hz, H-α), 5.36 (*q*, 2 H, *J* = 5 Hz and 11 Hz, H-2), 5.33 (*m*, 4 H, H-1″, H-2″, H-3″, H-4″), 4.41 (*m*, 2 H, H-6″, H-6‴), 4.08 (*m*, 1 H, H-5″), 2.57–3.25 (*m*, 2 H, H-3, H-3), 2.33 (*s*, 9 H, OAc-4′, 4‴, 5), 2.06 (*s*, 9 H, OAc-2″, 3″, 4″). MS: *m/e* 832 M$^+$ (rel. int. 1%), 790 (1), 748 (2), 477 (15), 435 (8), 356 (3), 331 (11), 315 (10), 314 (10), 272 (17), 271 (19), 229 (8), 189 (100), 169 (70), 164 (31), 147 (97), 127 (32), 120 (47), 109 (75), 95 (34), 70 (42), 43 (98).

Naringenin-7-O-β-D-glucoside (*prunin*). (^{13}C-NMR, DMSO-d_6, TMS int.) 197.2 ppm (C-4), 165.2 (C-7), 162.9 (C-5), 162.8 (C-9), 157.8 (C-4′), 128.8 (C-1′), 128.5 (C-2′, C-6′), 115.2 (C-3′, C-5′), 10.3.3 (C-10), 99.5 (C-1″), 96.5 (C-6), 95.4 (C-8), 78.7 (C-2), 77.1 (C-5″), 76.3 (C-3″), 73.1 (C-2″), 69.5 (C-4″), 60.6 (C-6″), 42.0 (C-3).

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AURMILLONE, A NEW ISOFLAVONE FROM THE SEEDS OF *MILLETTIA AURICULATA*

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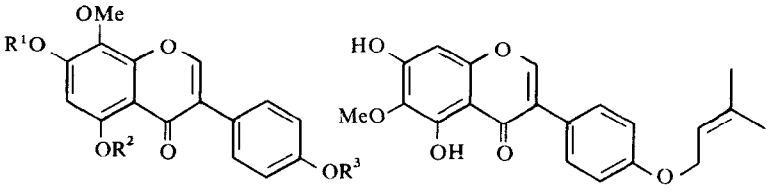
Key Word Index—*Millettia auriculata*; Leguminosae; auriculatin; sumatrol; auriculasin; new isoflavone; aurmillone.

Past work on roots of *Millettia anriculata* has yielded auriculatin, sumatrol [1], auriculin, isoauriculatin [2], while the leaves contain auriculasin, isoauriculasin and isoauriculatin [3]. We now report the structure determination of a new isoflavone, aurmillone (**1**), isolated from the seeds of *Millettia auriculata* (supplied by the United Chemical and Allied Products, Calcutta) along with auriculatin, sumatrol and auriculasin.

Aurmillone (**1**) mp 157–158° was analysed for $C_{21}H_{20}O_6$ and M$^+$ 368. Its phenolic nature is indicated by its solubility in alkali and green ferric colour. Its UV data (λ_{max}^{MeOH} nm (log ε) 268 (4.56), 332 (3.90)) [4], its IR data (ν $C{=}O_{CHCl_3}^{max}$ 1650 cm^{-1}) and low field singlet at 8.52 δ in its PMR spectrum (recorded in DMSO-d_6) is indicative of its isoflavone nature [4]. Further the UV spectral shifts—bathochromic shift of 268 nm band by 10 nm and 14 nm upon addition of $AlCl_3$–HCl and NaOAc respectively, suggests the presence of 5,7-dihydroxyisoflavone skeleton [4]. Aurmillone (**1**) formed a diacetate (**2**) mp 84–85°, $C_{25}H_{24}O_8$ and M$^+$ 452 (PMR (60 MHz, $CDCl_3$) two OCO$\underline{CH_3}$ at 2.32 δ 3H, *s*; 2.35 δ, 3H, *s*) on treatment with AC_2O–Py and a dimethyl ether (**3**), mp 124–126°, $C_{23}H_{24}O_6$ and M$^+$ 396, on refluxing for 48 hr with $Me_2SO_4|K_2CO_3|Me_2CO$. Aurmillone (**1**) formed a monomethyl ether (**4**) mp 124°, $C_{22}H_{22}O_6$ and M$^+$ 382 (PMR ($CDCl_3$) two O$\underline{CH_3}$ at 3.91 δ, 3H, *s*; 3.88 δ, 3H, *s*) on treatment with CH_2N_2. The monomethyl ether (**4**) exhibits UV data λ_{max}^{MeOH} 265 nm (log ε 4.52) and it underwent bathochromic shift by 10 nm upon addition of $AlCl_3$–HCl and gave green ferric colour. Therefore, it is concluded that the C_5 hydroxyl is not methylated. Thus in aurmillone (**1**), the presence of two hydroxyls one of which is chelated is confirmed.

The PMR spectrum of aurmillone (**1**) revealed a set of peaks (4.55 δ, 2H, *d*, *J* = 7 Hz, —O—$\underline{CH_2}$—; 5.55 δ, 1 H, *m*, =C$\underline{H}$—, and 1.78 δ, 6H, *br s*, =C($\underline{CH_3}$)$_2$) characteristic of *O*-3-methylbut-2-enyl group [2, 5]. The spectrum also revealed four aromatic protons constituting



(1) $R^1 = R^2 = H$; $R^3 = -CH_2-CH=CMe_2$
(2) $R^1 = R^2 = COMe$; $R^3 = -CH_2-CH=CMe_2$
(3) $R^1 = R^2 = Me$; $R^3 = -CH_2-CH=CMe_2$
(4) $R^1 = Me$; $R^2 = H$; $R^3 = -CH_2-CH=CMe_2$
(5) $R^1 = R^2 = R^3 = H$
(6) $R^1 = Me$; $R^2 = R^3 = H$
(7) $R^1 = R^2 = R^3 = Me$

(8)

A_2B_2 system (6.98 δ, 2H, *d*, $J = 9$ Hz; 7.50 δ, 2H, *d*, $J = 9$ Hz) assignable to *p*-disubstituted phenyl nucleus [4, 5], a high field aromatic singlet at 6.32 δ (1 H, *s*), a methoxyl group (3.80 δ, *s*, 3H), and two phenolic hydroxyls (8.39 δ, 1H, OH; 12.80 δ, 1H, *s*, chelated OH, both D_2O exchangeable).

Aurmillone (**1**) and its monomethyl ether (**4**) on acid hydrolysis (by heating with HOAc–HCl (19 : 1)) furnished, compound A (**5**), mp 240–241°, $C_{16}H_{12}O_6$ and M^+ 300, and compound B (**6**), mp 181°, $C_{17}H_{14}O_6$ and M^+ 314 respectively, both by loss of 3-methylbut-2-enyloxy group [5]. Alkaline hydrogen peroxide oxidation of aurmillone monomethyl ether (**4**) or dimethyl ether (**3**) furnished *p*-hydroxybenzoic acid which is presumably formed by the cleavage of 3-methylbut-2-enyl group under the alkaline conditions or during subsequent acidification [2]. Thus, two structures—5,7-dihydroxy-8-methoxy-4′-(3-methylbut-2-enyloxy) isoflavone (**1**) and 5,7-dihydroxy-6-methoxy-4′-(3-methylbut-2-enyloxy) isoflavone (**8**) were considered for aurmillone.

PMR solvent induced shifts [6–8] of aurmillone dimethyl ether (**3**) recorded in $CDCl_3$ and C_6H_6 (C_5-OCH$_3$ (3.98 δ in $CDCl_3$; 3.56 δ in C_6H_6, $\Delta = \delta\ CDCl_3 - \delta\ C_6H_6 = 25$ Hz), C_7-OCH$_3$ (3.95 δ or 3.92 δ in $CDCl_3$ 3.42 in C_6H_6, $\Delta = \delta\ CDCl_3 - \delta\ C_6H_6 = 32$ or 30 Hz), C_8-OCH$_3$ (3.92 δ or 3.95 δ in $CDCl_3$; 3.82 δ in C_6H_6 $\Delta = \delta\ CDCl_3 - \delta\ C_6H_6 = 6$ or 8 Hz)) reveal that an *ortho* proton is present to C_5-methoxyl group since it experiences large positive shift [7, 8]. In 5,6,7-trimethoxyflavone and 5,6,7,4′-tetramethoxyisoflavone the C_5-methoxyl group experiences negative shift of the order 1 to 7 Hz [8]. On the other hand C_5-OCH$_3$ of 5,7,8-trimethoxyflavone and 5,7,8,4′-tetramethoxyisoflavone (**7**) experience positive shift (~23 Hz) [8], which is comparable to that noticed in aurmillone i.e. 25 Hz. Therefore, structure 5,7,8-trioxygenated **3** rather than 5,6,7-trioxygenated was considered for aurmillone dimethyl ether.

The mps of compound A (**5**) its trimethyl ether (**7**) mp 138–139° $C_{19}H_{18}O_6$ and M^+ 342 and compound B (**6**) were found to be close to those of 5,7,4′-trihydroxy-8-methoxyisoflavone (**5**) [8, 9], 5,7,8,4′-tetramethoxyisoflavone (**7**) [8] and 5,4′-dihydroxy-7,8-dimethoxyisoflavone (**6**) [9] respectively and direct comparisons (mp, mmp, TLC and IR) revealed their identity. 5,7,8,4′-Tetramethoxyisoflavone (**7**) required for comparison was prepared by methylating authentic sample of **5** [8]. Thus, the structures **1**–**4** were assigned for aurmillone, its diacetate, dimethyl ether and monomethyl ether respectively. Mass spectral fragmentation of the compounds **1**–**7** are in conformity with the assigned structures [10, 11].

5,7 - Dihydroxy - 8 - methoxy - 4′ - (3 - methylbut - 2 - enyloxy)isoflavone structure (**1**) assigned to aurmillone (**1**) was further confirmed by the partial synthesis of its monomethyl ether (**4**) by the condensation of authentic **6** [9] with 3-methylbut-2-enyl bromide in Me_2CO–K_2CO_3–KI medium.

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